Electrochemistry of the Quasi-reversible Bis[2-ethyl-2-hydroxybutanoato(2−)]-oxochromate-(v) and -(iv) and Bis[2-hydroxy-2-methylbutanoato(2−)]oxochromate-(v) and -(iv) Redox Couples and the Crystal and Molecular Structure of Sodium Bis[2-ethyl-2-hydroxybutanoato(2−)]oxochromate(v)Sesquihydrate†

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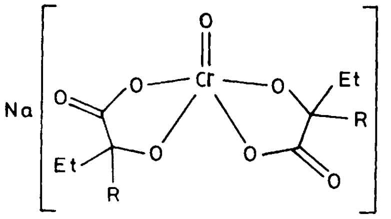
The Cr^V–Cr^{IV} redox couples of the complexes $[Cr(ehba)_2O]^{1-/2-}$ [ehba = 2-ethyl-2- hydroxybutanoate(2−)] and $[Cr(hmba)_2O]^{1-/2-}$ [hmba = 2-hydroxy-2-methylbutanoate(2−)]— exhibit quasi-reversible redox behaviour in both dimethyl sulphoxide (dmso) and dichloromethane. Solutions of the chromium(v) complex in dmso are stable for a year or more at room temperature, if they are stored in the dark. The chromium(iv) complex is much more reactive, but still has a lifetime on the minutes time-scale in dmso or CH_2Cl_2 under ambient conditions. The *X*-ray structure of $Na[Cr(ehba)_2O]\cdot1.5H_2O$ has been determined. It crystallises in the monoclinic space group *C*2/*c*, $a = 23.733(6)$, $b = 12.424(3)$, $c = 19.678(6)$ Å, $\beta = 108.30(3)°$, and $Z = 12$. The chromium complex has a distorted trigonal bipyramid of oxygen donor atoms, with the two carboxylate oxygens occupying the axial sites. The crystallographic analysis indicates that the reasons for the unusual stability of this complex and the reversibility of the Cr^V–Cr^{IV} redox couple lie, at least partially, in the steric protection that is caused by the ethyl substituents. Another important factor that leads to the high chemical stability of Cr^V in aprotic solvents, such as dmso and CH_2Cl_2, is that it is a weak oxidant in these solvents.

In the last two decades, many chromium(v) intermediates in the reduction of chromium(vi) compounds by organic substrates have been detected by the use of e.s.r. spectroscopy.[1] As well as the observation of these intermediates, a limited number of chromium(v) complexes have now been isolated and characterised.[2] They include the tetraoxochromate(v) ion, $[CrO_4]^{3-}$, which is stable in strongly alkaline media,[3] oxohalogeno complexes,[4] such as $[CrOX_4]^-$ and $[CrOX_5]^{2-}$, and complexes formed by the reactions of certain alcohols and salicylaldimines, that are resistant to oxidation.[5–8] One of the most stable classes of chromium(v) complexes is that obtained from the reaction of tertiary 2-hydroxyalkanoic acids with chromium trioxide,[9] and it is the chemical and electrochemical properties in non-aqueous solvents of two such complexes, $Na[Cr(ehba)_2O]$ (**1**) [ehba = 2-ethyl-2-hydroxybutanoate-(2−)] and $Na[Cr(hmba)_2O]$ (**2**) [hmba = 2-hydroxy-2-methylbutanoate(2−)] that are reported here.



R
(**1**) Et
(**2**) Me

The complex $[Cr(ehba)_2O]^-$ has been shown to have unusual stability for Cr^V,[9–12] and the redox couple Cr^V–Cr^{IV} is quasi-reversible in water, under certain conditions of pH.[13–16] The crystal structure of the complex $K[Cr(hmba)_2O]\cdot H_2O$, containing the ligand analogue where one of the ethyl substituents has been replaced by a methyl, has been reported.[10] The complex ion is sterically hindered in this structure and we have undertaken a structural study of $Na[Cr(ehba)_2O]\cdot1.5H_2O$ in order to see whether extra steric crowding could be a factor in increasing the chemical stability of (**1**) over (**2**).

Experimental

Solvents and Electrolytes.—Tetrabutylammonium tetrafluoroborate obtained from Aldrich or prepared from 40% aqueous tetrabutylammonium hydroxide (Aldrich) and tetrafluoroboric acid (Aldrich)[17] was recrystallised three times from hot ethyl acetate–diethyl ether.[18] Lithium perchlorate (Fluka, A.R. grade) was recrystallised three times from water.[19] Dimethyl sulphoxide (Merck) was freshly distilled at reduced pressure [≈2—3 mmHg (266—399 Pa), b.p. 50 °C] from NaOH pellets. Dichloromethane (Merck) was distilled from P_4O_{10}. Acetone (Merck) was refluxed (30 min) over $KMnO_4$ (Merck) and then distilled. Water was distilled before use.

Preparation of $Na[Cr(ehba)_2O]\cdot1.5H_2O$ *and* $Na[Cr(hmba)_2O]\cdot H_2O$.—These were synthesised by the standard procedure[9] from either 2-ethyl-2-hydroxybutanoic acid (Aldrich, 99%) or 2-hydroxy-2-methylbutanoic acid (Aldrich, 99%) and chromium(vi) oxide (Merck, A.R. grade) in acetone (Merck, A.R. grade). **CAUTION**: These complexes are mutagenic, cleave DNA rapidly *in vitro* and are potential carcinogens.[20] Due care should be taken to avoid both breathing the dust and allowing contact with the skin.

Chemical Stability of the Chromium(v) *Complexes in Non-aqueous Solvents.*—A cyclic voltammogram of a solution of $Na[Cr(ehba)_2O]\cdot1.5H_2O$ (5 mmol dm^{-3}) in dmso (containing 0.1 mol dm^{-3} NBu_4BF_4) was recorded. The solution was stored in the dark for 1.5 years and a second voltammogram was

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

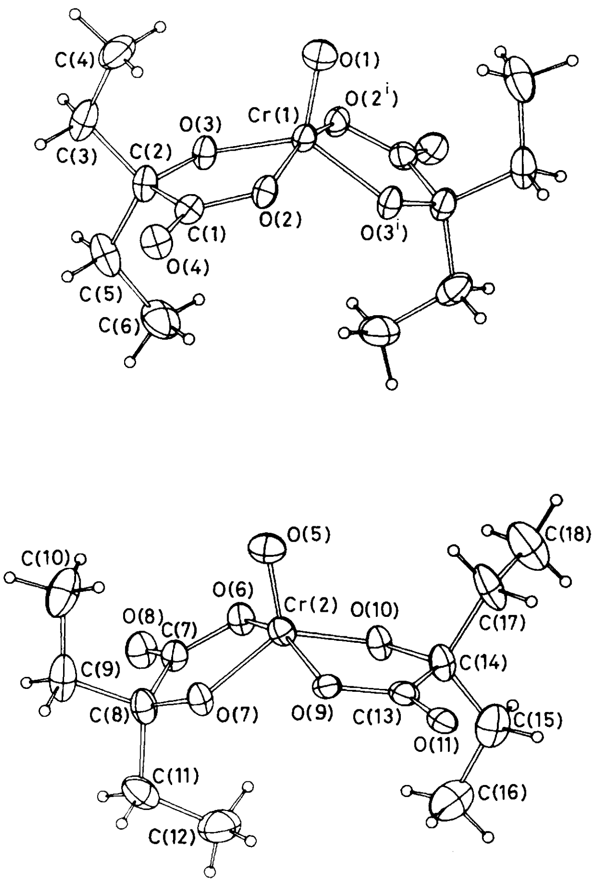


Figure 1. ORTEP plots of the two independent $[Cr(ehba)_2O]^-$ anions in $Na[Cr(ehba)_2O]\cdot1.5H_2O$. The superscript *i* indicates that the atoms are related by a two-fold rotation axis

recorded. It was found that approximately 40% of the original concentration of complex was still present in this solution.

Electrochemical Experiments.—These were performed using a three-electrode system incorporating a glassy carbon (BAS, diameter 2 mm) working electrode, a platinum wire auxiliary electrode, and a Ag–AgCl–KCl(saturated) reference electrode. A BAS-100 Electrochemical Analyzer was used in conjunction with an Osborne Executive microcomputer for data storage and a Houston HIPLOT DMP-40 digital plotter for recording the voltammograms. Standard BAS File Service software was used to transfer data from the BAS-100 to the IBM-compatible computer. 100% *iR* Compensation was applied to each experiment using the BAS software. In some experiments the electrochemistry was performed in the presence of neutral activated (400 °C, 1 h) alumina (Woelm).

Ferrocene (Fluka) was used as received, and all redox potentials were referenced to the ferrocenium–ferrocene redox couple.[21] All differential pulse experiments were performed under the following conditions: pulse amplitude = 50 mV; scan rate = 4 mV s^{-1}; sample width = 60 ms; pulse period = 1.000 s.

Crystal Growth.—Suitable cryatals of $Na[Cr(ehba)_2O]\cdot1.5H_2O$ were grown by slow vapour diffusion of pentane (Merck) into a concentrated solution of the sodium salt of the complex in acetone (Merck, A.R. grade).

Structure Determination.—*Crystal data.* $C_{12}H_{23}CrNaO_{8.5}$, M = 378.3, monoclinic, space group, $C2/c$, a = 23.733(6), b = 12.424(3), c = 19.678(6) Å, β = 108.30(3)°, U = 5 509(4) Å^3, D_c (Z = 12) = 1.368 g cm^{-3}, $F(000)$ = 2 376, $\mu(Mo\text{-}K_\alpha)$ = 6.30 cm^{-1}. Specimen: red prisms, 0.30 × 0.29 × 0.25 mm. N = 4 879, N_o = 2 988, $[I > 2.5\sigma(I)]$ range of *hkl* 0 to 27, 0 to 14, −22 to 22, merging R = 0.009, R = 0.048, R' = 0.055, $w = 3.9/[\sigma^2(F_o) + 0.000\,16\,F_o{}^2]$ residual extrema ±0.35 e Å^{-3}.

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf–Nonius CAD4-F diffractometer within the limit $2\theta_{max.}$ = 50°, with Mo-K_α radiation, λ = 0.710 69 Å, graphite monochromator, and operating in the ω—θ mode. Data were reduced and Lorentz, polarisation and decomposition (25%) corrections were applied using a local data reduction program. The structure was solved by direct methods followed by Fourier syntheses, and was refined by full-matrix least-squares analysis with SHELX 76.[22] There is extensive disorder of water molecules in a region of the structure. These were refined with a group thermal parameter and variable occupancy factors. All non-hydrogen atoms with the exception of the minor contributors to the disordered atoms were refined anisotropically. Hydrogen atoms were included at calculated sites (C–H 0.97 Å) and refined with isotropic group thermal parameters. A peak of *ca.* 0.5 e Å^{-3} in height was observed *ca.* 1.9 Å from Cr(2) and *trans* to the oxo group O(5). Given that six-co-ordination is feasible a partial oxygen O(5′) was refined at this site giving an occupancy of 4%. The resulting geometry about Cr(2) and involving O(5) is not that expected for a six-co-ordinate complex; however, rearrangement of the complex would be expected on co-ordination of a sixth oxygen. Thus, we cannot rule out completely the possibility of a six-co-ordinate complex being a minor contributor to the Cr(2) site. An alternative explanation for this peak is disorder of the oxo group on each side of the Cr(2) atom. The refinement and structure parameters are essentially unchanged whether or not this peak is considered to be real. Scattering factors and anomalous dispersion corrections for Cr were taken from ref. 23 and for all other atoms the values supplied in SHELX 76 were used. Non-hydrogen atom co-ordinates are listed in Table 1 and selected bond distances and angles in Table 2. The atomic nomenclature is defined in Figure 1.[24]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results

The Structure of $Na[Cr(ehba)_2O]\cdot1.5H_2O$.—The structure consists of two complex anions, one lying on a two-fold rotation axis at $x = \frac{1}{2}$, $z = \frac{3}{4}$ and the other at a general site, two sodium cations, one at a centre of symmetry ($\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$) and the other at a general site, one full-occupancy water molecule and 1.25 water molecules disordered over six sites. (The stoicheiometry in the formula arises because there are 1.5 Cr anions per 2.25 water molecules when the relative occupancy of the different anions is taken into account.) There are two hydrogen bonds between the full-occupancy water molecule and O(2) and O(3) of the complex on the two-fold axis (2.872 and 2.849 Å). The sodium atom at a centre of symmetry is weakly bonded to six oxygen atoms of the two complexes (2.728, 2.723, and 2.323 Å) and that at the general site is involved in seven weak bonds, six to oxygen atoms of the complexes (2.430—2.602 Å) and one to the full-occupancy water molecule (2.285 Å).

The geometries of the two complex anions are similar (Figure 1), each Cr atom being bonded to an oxo group and two bidentate ehba dianions *via* carboxylate- and alkanolate-derived

Table 1. Positional parameters for $Na[Cr(ehba)_2O]\cdot1.5H_2O$

Atom	*x*	*y*	*z*
Cr(1)	0.5000	0.389 8(1)	0.7500
O(1)	0.5000	0.514 3(4)	0.7500
O(2)	0.418 0(1)	0.361 4(2)	0.703 2(2)
O(3)	0.508 8(1)	0.330 1(3)	0.670 9(1)
O(4)	0.353 5(1)	0.303 7(3)	0.602 6(2)
C(1)	0.404 2(2)	0.322 5(4)	0.638 8(2)
C(2)	0.456 9(2)	0.305 5(4)	0.612 0(2)
C(3)	0.453 2(3)	0.380 5(5)	0.549 6(3)
C(4)	0.441 8(3)	0.498 1(6)	0.563 8(3)
C(5)	0.459 3(2)	0.188 9(5)	0.590 3(3)
C(6)	0.465 1(3)	0.109 1(5)	0.648 0(4)
Cr(2)	0.237 9(1)	0.092 3(1)	0.816 9(1)
O(5)	0.188 5(2)	0.157 2(3)	0.835 1(2)
O(5′)	0.293 9(17)	0.008 5(31)	0.789 7(20)
O(6)	0.253 0(1)	0.178 7(2)	0.744 8(2)
O(7)	0.211 2(1)	−0.003 2(2)	0.745 4(1)
O(8)	0.240 2(2)	0.190 0(3)	0.628 9(2)
O(9)	0.245 7(1)	−0.029 7(2)	0.877 8(2)
O(10)	0.310 9(1)	0.122 3(2)	0.874 2(1)
O(11)	0.298 0(2)	−0.093 8(3)	0.983 6(2)
C(7)	0.234 9(2)	0.140 0(4)	0.679 8(2)
C(8)	0.207 9(2)	0.028 1(4)	0.674 3(2)
C(9)	0.144 4(3)	0.030 3(5)	0.626 4(3)
C(10)	0.106 0(3)	0.106 6(6)	0.653 1(4)
C(11)	0.244 5(3)	−0.050 7(4)	0.645 2(3)
C(12)	0.309 0(3)	−0.058 5(6)	0.689 7(4)
C(13)	0.290 6(2)	0.026 5(4)	0.436 4(2)
C(14)	0.330 8(2)	0.068 8(4)	0.941 1(2)
C(15)	0.393 7(3)	0.032 1(5)	0.953 7(3)
C(16)	0.402 0(3)	−0.046 1(7)	0.901 4(4)
C(17)	0.323 7(3)	0.144 6(4)	1.000 5(2)
C(18)	0.358 3(4)	0.247 5(6)	1.009 8(4)
Na(1)	0.2500	0.2500	0.5000
Na(2)	0.189 9(1)	0.169 8(1)	0.297 3(1)
OW(1)	0.372 6(2)	0.258 4(5)	0.805 9(3)
OW(2)	0	0.315 2(30)	0.7500
OW(3)	0.487 7(12)	0.198 7(19)	0.195 7(19)
OW(4)	0.446 9(11)	0.201 2(26)	0.248 3(17)
OW(5)	0.490 4(12)	0.200 0(23)	0.141 9(19)
OW(6)	0.460 2(16)	0.118 2(34)	0.268 9(19)
OW(7)	0.447 6(12)	0.238 6(20)	0.199 5(15)

Table 2. Bond lengths (Å) and angles (°) for the anionic complexes in $Na[Cr(ehba)_2O]\cdot1.5H_2O$

O(1)–Cr(1)	1.547(5)	O(2)–Cr(1)	1.905(3)
O(3)–Cr(1)	1.796(3)	C(1)–O(2)	1.300(5)
C(2)–O(3)	1.434(5)	C(1)–O(4)	1.214(5)
C(2)–C(1)	1.516(6)	C(3)–C(2)	1.522(6)
C(5)–C(2)	1.516(7)	C(4)–C(3)	1.527(8)
C(6)–C(5)	1.482(8)	O(5)–Cr(2)	1.557(3)
O(5′)–Cr(2)	1.89(4)	O(6)–Cr(2)	1.900(3)
O(7)–Cr(2)	1.798(3)	O(9)–Cr(2)	1.904(3)
O(10)–Cr(2)	1.784(3)	C(7)–O(6)	1.307(5)
C(8)–O(7)	1.430(5)	C(7)–O(8)	1.218(5)
C(14)–O(10)	1.417(5)	C(8)–C(7)	1.520(6)
C(9)–C(8)	1.506(7)	C(11)–C(8)	1.533(7)
C(10)–C(9)	1.519(9)	C(12)–C(11)	1.509(8)
C(15)–C(14)	1.507(8)	C(17)–C(14)	1.549(7)
C(16)–C(15)	1.473(9)	C(18)–C(17)	1.499(8)
O(2)–Cr(1)–O(1)	100.7(1)	O(3)–Cr(1)–O(1)	114.4(1)
O(3)–Cr(1)–O(2)	83.3(1)	C(1)–O(2)–Cr(1)	116.5(3)
O(2)–Cr(1)–O(2)	158.7(2)	C(2)–O(3)–Cr(1)	119.0(2)
O(3)–Cr(1)–O(3)	131.1(2)	O(4)–C(1)–O(2)	122.9(4)
C(2)–C(1)–O(2)	114.1(4)	C(2)–C(1)–O(4)	122.9(4)
C(1)–C(2)–O(3)	106.4(3)	C(3)–C(2)–O(3)	109.9(4)
C(3)–C(2)–C(1)	110.4(4)	C(5)–C(2)–O(3)	109.4(4)
C(5)–C(2)–C(1)	109.8(4)	C(5)–C(2)–C(3)	110.8(4)
C(4)–C(3)–C(2)	114.0(4)	C(6)–C(5)–C(2)	115.2(4)
O(6)–Cr(2)–O(5)	102.2(2)	O(7)–Cr(2)–O(5)	114.6(2)
O(7)–Cr(2)–O(6)	83.7(1)	O(9)–Cr(2)–O(5)	101.5(2)
O(9)–Cr(2)–O(6)	156.2(1)	O(9)–Cr(2)–O(7)	84.7(1)
O(10)–Cr(2)–O(5)	113.5(2)	O(10)–Cr(2)–O(6)	88.9(1)
O(10)–Cr(2)–O(7)	131.8(1)	O(10)–Cr(2)–O(9)	83.4(1)
C(7)–O(6)–Cr(2)	116.3(3)	C(8)–O(7)–Cr(2)	118.9(3)
C(14)–O(10)–Cr(2)	117.5(2)	O(8)–C(7)–O(6)	122.0(4)
C(8)–C(7)–O(6)	114.0(4)	C(8)–C(7)–O(8)	124.0(4)
C(7)–C(8)–O(7)	106.7(4)	C(9)–C(8)–O(7)	110.7(4)
C(9)–C(8)–C(7)	110.1(4)	C(11)–C(8)–O(7)	109.1(4)
C(11)–C(8)–C(7)	109.6(4)	C(11)–C(8)–C(9)	110.6(5)
C(10)–C(9)–C(8)	112.8(5)	C(12)–C(11)–C(8)	114.5(5)
C(15)–C(14)–O(10)	108.5(4)	C(17)–C(14)–O(10)	109.4(4)
C(17)–C(14)–C(15)	113.3(5)	C(16)–C(15)–C(14)	115.3(5)
C(18)–C(17)–C(14)	115.2(5)		

oxygen atoms. The geometry about the Cr atoms is intermediate between square pyramidal, in which the oxo group occupies the apical site, and trigonal bipyramidal in which the carboxylate oxygen atoms occupy the apical sites. The latter description is probably the more valid since the Cr(2) atom lies only 0.03 Å out of the equatorial plane, but the O_{ax}–Cr–O_{ax} angle is 156.9(1)°. The atoms defining the basal plane in the square pyramidal description deviate by >0.16 Å from the plane. A similar geometry was observed in the structure of $K[Cr(hmba)_2O]\cdot H_2O$.[10] In both complex anions, two ethyl groups are folded back toward the Cr atom on the side opposite to the oxo group. For the complex lying on the two-fold axis, the other two ethyl groups are folded toward the oxo group and in the other complex one is folded toward the oxo group, but the other is folded away. Distances between the oxo group and the ethyl groups and between the ethyl groups themselves are close to those expected on the basis of van der Waals contacts (C ··· O > 3.558, C ··· C > 3.830, and H ··· H > 2.51 Å).

The Cr–O(oxo) distances [1.547(5) and 1.557(3) Å] are similar to that observed in $K[Cr(hmba)_2O]\cdot H_2O$ [1.554(14) Å].[10] There are differences of greater than 0.1 Å between the Cr to carboxylate oxygen bond lengths [1.900(3)—1.905(3) Å] and the Cr to alkanolate-derived oxygen bond lengths [1.784(3)—1.798(3) Å].

Least-squares planes calculations show that the O_2CCO groups of the ligands are planar to within 0.05 Å and that the Cr atoms lie 0.10—0.27 Å out of these planes.

Chemical Stability of the Chromium(V) *Complexes in Non-aqueous Solvents.*—Electrochemical experiments performed on the complex $[Cr(ehba)_2O]^-$ in dmso show that the half-life of this complex at ambient conditions is a year or more, if kept in the dark. Although similar experiments have not been performed in dichloromethane, it has been observed to be stable over a matter of weeks in this solvent. This is in marked contrast with the results obtained in both water, even under the optimum conditions of pH, and acetone.[9–12]

Electrochemistry. Quasi-reversible redox behaviour was observed in the cyclic voltammograms of the Cr^V–Cr^{IV} couple of $Na[Cr(ehba)_2O]\cdot1.5H_2O$ or $Na[Cr(hmba)_2O]\cdot1.5H_2O$ in both dichloromethane and dmso (*e.g.* Figure 2). Under the same conditions, the ferrocenium–ferrocene couple exhibited close to reversible behaviour, which indicated that the observed peak-to-peak separations in the cyclic voltammograms of the chromium complex were not due to uncompensated resistance. In acetone, the reduction was irreversible until scan rates of

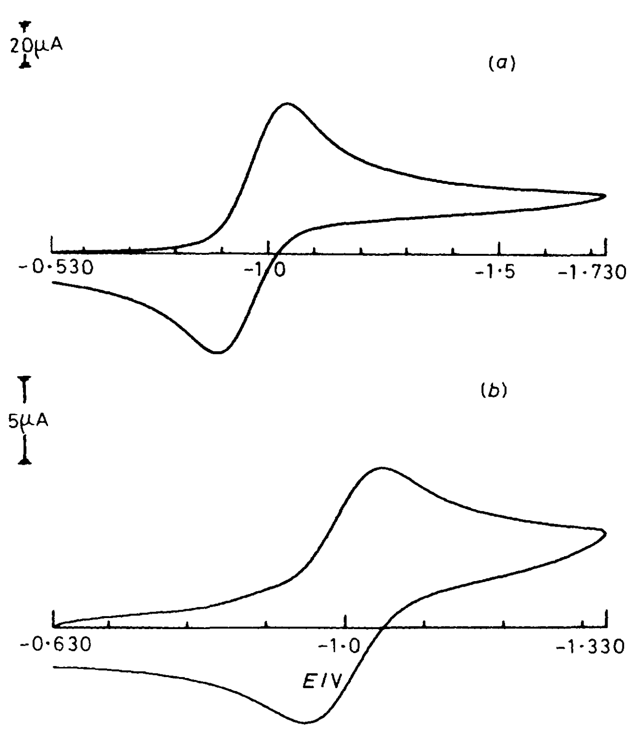


Figure 2. Cyclic voltammograms of (*a*) Na[Cr(ehba)$_2$O]$\cdot$1.5H$_2$O (8.8 mmol dm^{-3}) and (*b*) Na[Cr(hmba)$_2$O]$\cdot$H$_2$O (2.5 mmol dm^{-3}) in dmso with 0.1 mol dm^{-3} NBu$_4$BF$_4$ as the background electrolyte; v = 100 mV s^{-1}; referenced against ferrocenium–ferrocene; 100% compensated for *iR* drop

$\geqslant$1 000 mV s^{-1} were attained unless the electrochemistry was performed after addition of the solvent to freshly activated alumina. At scan rates $\geqslant$1 000 mV s^{-1}, or in the presence of activated alumina even at slow scan rates, the electrochemistry became quasi-reversible (Figure 3). Consistent with previous observations on the aqueous electrochemistry,[13,14] both of the chromium(v) complexes were most reversible at pH values between 3 and 4. In acetone, the ehba complexes were more chemically stable[9] and more reversible in their reductions than their hmba counterparts. The redox data are summarised in Table 3. It is clear from these results that the chromium(v) complexes are much more powerful oxidants (by *ca.* 1 V) in water than in dmso and dichloromethane.

In addition to the reduction process, irreversible oxidation processes were observed in both acetone and dichloromethane. No reversibility was observed in these multi-electron processes at the highest scan rate (50 000 mV s^{-1}) employed in these experiments. The oxidation process is illustrated in the cyclic voltammogram observed for [Cr(hmba)$_2$O]$^-$ in acetone (Figure 4). No other oxidation or reduction processes are observed in the potential ranges that are accessible in these solvents.

Discussion

On chemical grounds, one would expect the Cr–O(alkanolate) bonds to be shorter than the Cr–O(carboxylate) bonds, since a deprotonated alcohol ligand is a better σ donor than a carboxylate ligand, and this is what is observed in the structure. In the trigonal bipyramidal description, the alkanolate oxygens occupy the equatorial positions along with the oxo oxygen. This is not surprising since it is these three groups that have the largest steric demands. A very similar geometric arrangement was observed in the structure of K[Cr(hmba)$_2$O]$\cdot$H$_2$O, but no

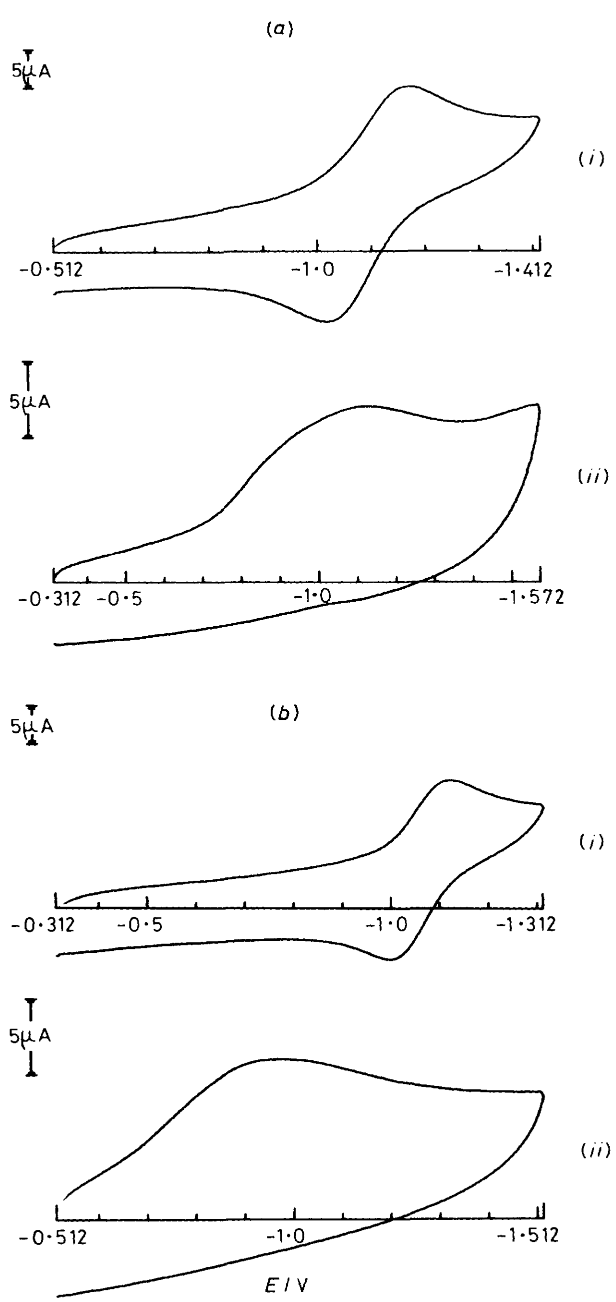


Figure 3. Cyclic voltammograms of (*a*) Na[Cr(ehba)$_2$O]$\cdot$1.5H$_2$O (2.1 mmol dm^{-3}) in acetone and (*b*) Na[Cr(hmba)$_2$O]$\cdot$H$_2$O (4.1 mmol dm^{-3}) in acetone (*i*) with and (*ii*) without neutral alumina added to remove traces of water; in all cases with 0.1 mol dm^{-3} NBu$_4$BF$_4$ as the background electrolyte. Other details as in Figure 2

explanation was put forward.[10] Longer bonds to the atoms which occupy the apical sites of a trigonal bipyramidal description are expected, because these sites are the more sterically crowded. However, the bond length difference is perhaps larger than one might expect from steric effects alone and supports the notion that the alkanolate groups are better σ donors than the carboxylate groups.

Most of the differences in bond lengths and bond angles within the structures of the complex ions contained in Na[Cr(ehba)$_2$O]$\cdot$1.5H$_2$O and K[Cr(hmba)$_2$O]$\cdot$H$_2$O are insignificant. However, the average O–Cr–O bond angle (101.3°) involving the oxo and carboxylate oxygens is significantly less (1°) in the structures of the ehba complexes as compared to the

Table 3. Reduction potentials for the Cr^{V}–Cr^{IV} couples of $Na[Cr(ehba)_2O]$ and $Na[Cr(hmba)_2O]$ at ν = 100 mV s^{-1}

Solvent	$E_f{}^a$/V	E_a/V	i_a/μA	E_c/V	i_c/μA	ΔE_p/V	i_a/i_c	$[Cr^V]$/mmol dm^{-3}
(*a*) ehba								
Water (pH 4.1)	0.00	+0.04	15	−0.04	13	0.08	1.10	2.4
Acetone[b]	−1.14	−1.11	24	−1.18	23	0.07	0.96	2.5
CH_2Cl_2	−1.09	−1.04	21	−1.13	23	0.09	0.90	2.2
Me_2SO	−0.97	−0.93	9	−1.01	13	0.08	0.68	2.3
(*b*) hmba								
Water (pH 4)	−1.10	0.02	1	0.17	11	0.15	0.13	2.0
Acetone	−1.09	−1.04	17	−1.14	18	0.11	0.97	1.0
CH_2Cl_2	−1.03	−0.99	18	−1.06	21	0.07	0.85	2.1
Me_2SO	−0.94	−0.89	6	−0.99	7	0.10	0.89	2.5

[a] *vs.* Ferrocenium–ferrocene. [b] In the presence of freshly activated alumina.

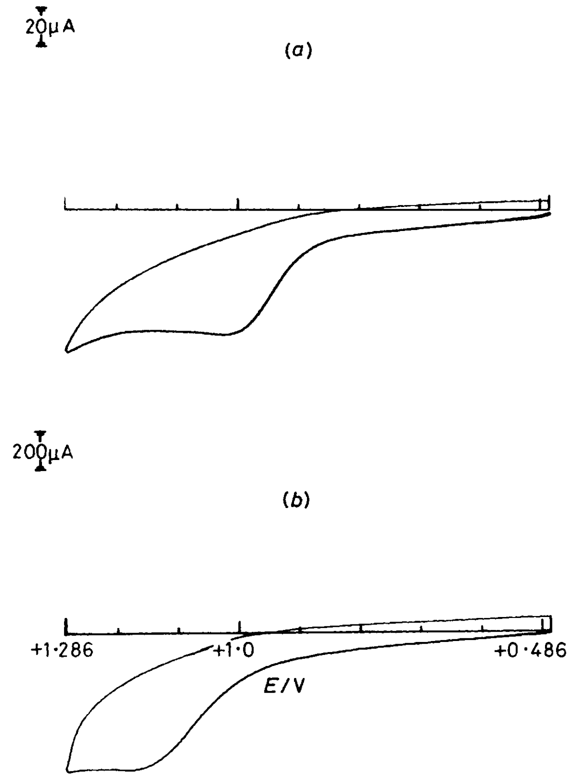
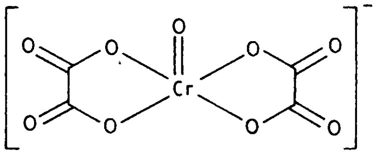


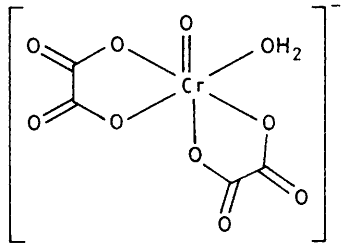
Figure 4. Cyclic voltammograms of the oxidation process observed in acetone with 0.1 mol dm^{-3} NBu_4BF_4 as the background electrolyte for the Cr^{VI}–Cr^{V} couple of $Na[Cr(hmba)_2O]\cdot H_2O$ at ν = 100 (*i*) and 10 240 mV s^{-1} (*ii*). Other details as in Figure 2

hmba complex. This may be indicative of a small degree of extra steric compression of this bond angle that is induced by the bulkier ligand. This difference is probably too small to explain the enhanced chemical stability of the ehba complex over the hmba complex, but the steric differences will be more pronounced in the activated state if the ligand substitution reaction goes *via* an associative mechanism. Despite this, the complexes have been shown to undergo rapid (seconds time-scale) ligand exchange[15] and therefore the chemical stability cannot be accounted for by the rate of substitution of the ligands. A corollary to this observation is that the steric factors must increase the thermodynamic stability of the complex.

In less sterically hindered chromium(V) complexes, such as the oxalato complex, a considerable amount of electrochemical and e.s.r. spectroscopic data has been obtained which has shown the presence of two chromium(V) complexes in equilibrium.[14,15,25,26] The evidence now obtained indicates that these complexes are the five- and six-co-ordinate forms of the bis(oxalato) complex, (**3**) and (**4**), respectively.[14,15,26] By contrast, the ehba complex only shows the e.s.r. signal that is indicative of a five-co-ordinate complex.[26] Similar observations have been made in dmso and dichloromethane.[27] It is apparent that steric interactions push the equilibrium between the five- and six-co-ordinate forms almost entirely towards the five-co-ordinate complex for the ehba and hmba ligands.



(**3**)



(**4**)

The five-co-ordinate form is believed to be more stable towards reduction. Obviously, the more steric bulk that can be introduced into the ligands, then the more this equilibrium is pushed towards the five-co-ordinate form and this may be the reason for the enhanced chemical stability of $[Cr(ehba)_2O]^-$ over $[Cr(hmba)_2O]^-$.

Apart from the steric factors that have been mentioned above, another important contribution to the stability of these chromium(V) complexes is the influence of outer-sphere solvation. Hydrogen bonding of solvent molecules to the five anionic donor groups (similar to that observed in the crystal structure) tends to stabilise the chromium(IV) oxidation state in comparison to Cr^V, because the co-ordinated ligands are more basic in the lower oxidation state. This results in the large negative shifts in the Cr^{V}–Cr^{IV} redox potentials that are observed in aprotic solvents such as dmso in comparison to solvents that are strong hydrogen-bonding acids, such as water.[16,28] Therefore, the extreme chemical stability of the chromium(V) complexes in solvents such as dmso probably arises from a combination of factors. These may include a greater resistance to co-ordination of the bulkier dmso solvent molecule in comparison to water, and the observation that the chromium(V) complexes are very weak oxidants in dmso and dichloromethane and are not able to oxidise the ligand. The fact that dichloromethane is a poorly co-ordinating solvent does not play a part in the stability of **(1)** and **(2)** in this solvent, since these complexes are extremely stable in dmso, which is a co-ordinating solvent. The sensitivity of the electrochemistry of the chromium(V) complexes to traces of water in acetone is not understood, as yet. This aspect needs further investigation especially in the light of the small affect that traces of water have in other solvents such as dmso.

The oxidation behaviour of the complexes probably involves an initial one-electron oxidation to Cr^{VI} followed by a rapid oxidation of the ligand and/or solvent. There is no reason to suspect that a five-co-ordinate geometry for a chromium(VI) complex is inherently unstable since five- and six-co-ordination is common in isoelectronic vanadium(V) chemistry and chromium(VI) complexes of co-ordination numbers greater than four are thought to be the intermediates in the oxidations of organic and inorganic substrates by Cr^{VI}.[1] Therefore, the likely reason for the instability of the chromium(VI) complexes is that there is a low-energy pathway for oxidation of the ligand or solvent, probably involving either hydride abstraction by the $Cr^{VI}=O$ group or an oxo transfer reaction.

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